

# Octa-, Hexa-, and Tetracoordination in Tin(IV) Derivatives of *cis*- $\beta$ -(Methylthio)stilbene- $\alpha$ -thiol

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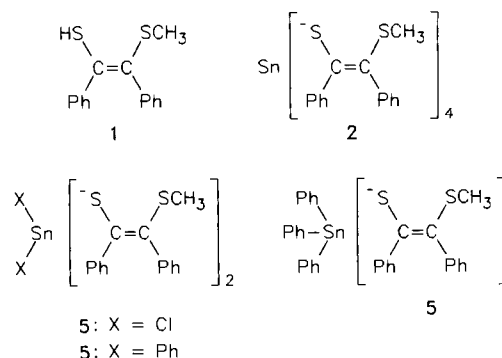
The *S*-methyl-*cis*-stilbene- $\alpha,\beta$ -dithiolate of Sn(IV),  $\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_4$ , has an octacoordinate structure with two sets of four covalent and coordinate Sn-S and Sn-S(CH<sub>3</sub>) bonds of 2.425(3) and 3.599(3) Å, respectively. Both types of Sn-S bonds are close to being tetrahedral, the coordination geometry is a distorted cube. This unprecedented structure appears to involve conventional covalent and outer-sphere coordinative Sn-S bonds. In the diphenyl derivative  $\text{Ph}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  the  $\text{SnC}_2\text{S}_2$  core formed by the covalent Sn-C

and Sn-S(thiolato) bonds is tetrahedral, but two coordinate outer-sphere Sn-S(CH<sub>3</sub>) bonds of 3.500(3) Å are also present. In the related  $\text{SnCl}_2[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  the presence of the polar Sn-Cl bonds prevents outer-sphere bonding; the coordination geometry is distorted octahedral. In the triphenyltin derivative  $\text{Ph}_3\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]$  the coordination geometry is tetrahedral, the thiol-thioether ligand being monodentate with the SCH<sub>3</sub> group in a non-interactive position.

The concept of second- or outer-sphere coordination, originally introduced by Alfred Werner<sup>[1]</sup>, has played a major role in the subsequent development of the theory of bonding in metal complexes and has recently re-emerged as a means of describing higher order bonding interactions in complexes with crown ether ligands and in systems involving supramolecular or host-guest interactions<sup>[2]</sup>. In molecular compounds, the preference for inner- over outer-sphere coordination may be expected to be dependent primarily on the size of the central atom, the symmetries and energies of the available unoccupied orbitals, electronegativity differences and on structural details of the ligating groups. Accordingly, with certain metals and ligands complexes with unusual coordination numbers and geometries are obtained, but because of the multifactorial nature of the metal-ligand interactions, predictions as to the behavior of a given metal or ligand are not generally possible. In the course of our ongoing studies of metal complexes with unsaturated thiol-thioether ligands<sup>[3,4]</sup> notably of *cis*- $\beta$ -(methylthio)stilbene- $\alpha$ -thiol,  $\text{Ph}(\text{SCH}_3)\text{C}=\text{C}(\text{SH})\text{Ph}$  (**1**) we became interested in the corresponding derivatives of tin, an element whose growing biological importance<sup>[5]</sup> is believed to be associated with its high affinity for biogenic thiol ligands. In general, tin(IV) is known to form compounds or complexes in which it adopts the coordination numbers 4 and 6, although compounds with coordination numbers 2, 3, 5, 7, and 8 are also known<sup>[6]</sup>. Higher coordination numbers are favored in compounds with electronegative substituents, although even in the organotin derivatives containing covalent  $\text{R}_2\text{Sn}$  and  $\text{RSn}$  groups, hexa- and heptacoordination is still possible. However, while the derivatives with  $\text{R}_3\text{Sn}$ - may still be pentacoordinated, no hexacoordinated compounds of this type are known<sup>[7]</sup>. In complexes of Sn(IV) with sulfur ligands such as dithiocarbamates, xanthates, and dithiophosphinates,

penta- and hexacoordinated structures are preferred over tetracoordination<sup>[8,9]</sup> due to the polarity of the Sn-S bond. Octacoordination could not yet be demonstrated with these ligands. In the complex  $\text{Sn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4$ , for example, the coordination number of tin is only 6, as two of the dithiocarbamate ligands adopt a monodentate coordination mode<sup>[10]</sup>.

Unsaturated thiol-thioethers are facultative mono-, bidentate, and  $\mu$ -S-bridging ligands<sup>[11]</sup>.



In mononuclear complexes of **1**, the unsaturated thioether-thiol ligands may be monodentate with a non-interacting-SCH<sub>3</sub> group or bidentate. Intermediate structures are also realized in which the coordinative M:S bond is significantly elongated, suggesting outer-sphere bonding interactions. In this paper we show that this is the case in the Sn(IV) complex of **1** of composition  $\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_4$  (**2**). In addition, we also describe the structures of the related compounds  $\text{Cl}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (**3**),  $\text{Ph}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (**4**), and  $\text{Ph}_3\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]$  (**5**), which were prepared for comparative purposes.

## Results and Discussion

Complex **2** was obtained by the aerobic reaction of  $\text{SnCl}_2$  with **1** in aqueous ethanol. It may be assumed that in this reaction Sn(II)-thiolato species are initially formed which are rapidly converted to the tin(IV) compound **2**. The complexes **3**, **4**, and **5** were obtained in reactions not requiring an oxidative step by combining solutions of **1** with  $\text{SnCl}_4$ ,  $\text{Ph}_2\text{SnCl}_2$ , and  $\text{Ph}_3\text{SnCl}$ , respectively. Complexes **2**, **3** and **4** form red-orange to yellow, crystalline solids, **5** is colorless; all compounds are air-stable, insoluble in water but readily soluble in aprotic organic solvents. Since metal complexes of thiol-thioethers frequently show structurally dynamic behavior in solutions<sup>[3,4]</sup>,  $^1\text{H-NMR}$  measurements were conducted on solutions of complexes **2–5** in  $\text{CDCl}_3$  at different temperatures. However, in the temperature range of  $\pm 50^\circ\text{C}$  only singlets of the *S*-methyl protons were observed, and no features suggesting dynamic behavior emerged on a more detailed analysis of the spectra. While this indicates that, in this instance,  $^1\text{H-NMR}$  spectra allow no distinction between the different ligand binding modes, on-off equilibria involving the ligand  $\text{SCH}_3$  groups are still possible as these could be established rapidly beyond the NMR time scale.

The structures of complexes **2–5** in the solid state revealed unusual features due to the presence of covalent and coordinative Sn–S bonds in the same molecule. Compound **2** crystallizes in a tetragonal space group (see Table 1) and contains octacoordinated Sn(IV) with two sets of essentially tetrahedral Sn–S bonds. The coordination polyhedron is a distorted cube (see Figures 1, 2, Table 2). The S–Sn–S bond angles of the covalent Sn–S bonds are 107 and  $114.5^\circ$ , respectively, indicating only a small deviation from ideal tetrahedral symmetry; the S–Sn–S angles of the coordinate Sn–S bonds of 80.1 and  $125.9^\circ$  are more distorted. The

Table 1. Crystallographic data collection parameters of complexes **2–5**

	2 <sup>a)</sup>	3 <sup>a)</sup>	4	5
Empirical Formula	$\text{C}_6\text{H}_5\text{S}_2\text{Cl}_2\text{S}_8\text{Sn}$	$\text{C}_{31}\text{H}_{28}\text{Cl}_4\text{S}_4\text{Sn}$	$\text{C}_4\text{H}_3\text{S}_6\text{S}_4\text{Sn}$	$\text{C}_{33}\text{H}_{28}\text{S}_2\text{Sn}$
Crystal System	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	$I4_1/a$	$P2_1/c$	$C2/c$	$P2_1/c$
<i>a</i> , Å	19.971(3)	8.177(3)	17.815(6)	9.545(5)
<i>b</i> , Å		35.144(8)	8.818(4)	32.701(2)
<i>c</i> , Å	15.242(3)	12.281(4)	24.546(7)	9.849(8)
$\beta$ , deg.		107.80(3)	104.90(3)	107.03(6)
<i>V</i> , Å <sup>3</sup>	6079(2)	3360(2)	3726(2)	2939(4)
<i>Z</i>	4	4	4	4
Formula Weight	1231	704.4	787.6	607.4
<i>D</i> (calcd), g cm <sup>-3</sup>	1.345	1.56	1.404	1.373
Cryst. size, mm	.25x.25x.35	.19x.33x.64	.11x.19x.44	.14x.25x.30
$\mu$ , mm <sup>-1</sup>	0.809	1.34	0.930	1.03
$\lambda$ , MoK $\alpha$	0.71073	0.71073	0.71073	0.71073
<i>T</i> , (K)	297	173	297	297
$2\theta$ Range, °	4.0–50.0	4–50.0	4–45.0	4–45.0
<i>F</i> (000)	2520	1584	1608	1232
Reflectns. measured	3184	6091	3042	4150
Independent reflectns.	2687	5604	2765	3816
<i>R</i> <sub>int</sub> , %	0.00	1.68	1.76	3.11
Reflectns. w. $F > 6.0\sigma(F)$	1909	4453	1984	2587
No. of parameters	162	361	213	325
<i>R</i> ( <i>F</i> ), w <i>R</i> ( <i>F</i> ) <sup>b)</sup>	0.031, 0.052	0.040, 0.059	0.026, 0.099	0.041, 0.071

<sup>a)</sup> With one molecule of  $\text{CH}_2\text{Cl}_2$  of crystallization. — <sup>b)</sup>  $R = (\sum \|F_o\| - |F_c|) / \sum \|F_o\|$ ;  $wR = [(\sum (F_o - |F_c|)^2) / \sum (F_o)^2]^{1/2}$ .

covalent Sn–S bonds have the length of 2.436(1) Å, which is normal for Sn(IV)-thiolato derivatives and closely corresponds to the sum of the covalent radii of 2.44 Å<sup>[12]</sup> and may be viewed as conventional equivalent tetrahedral Sn–S bonds involving the 5s and 5p orbitals. The coordinate Sn–S(CH<sub>3</sub>) bonds with a length of 3.599(2) Å are significantly shorter than the sum of the van der Waals radii (3.97 Å<sup>[12]</sup>) and could involve orbitals 6s and 6p of Sn.

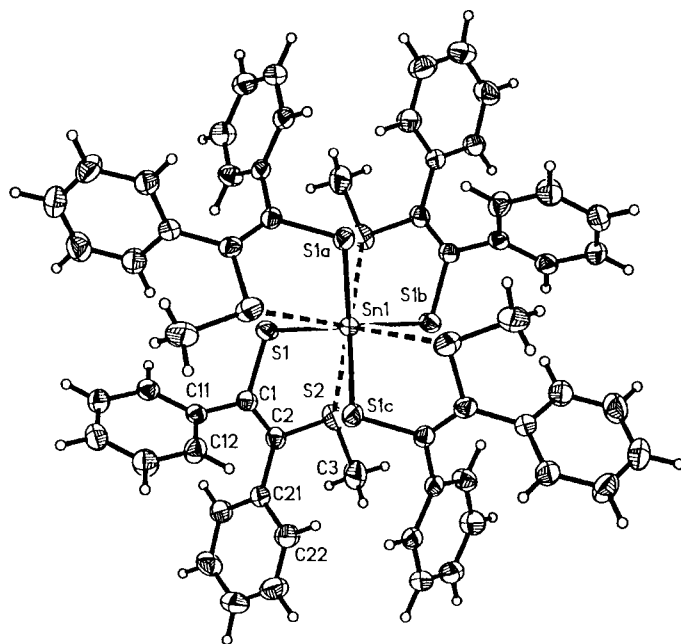


Figure 1. Perspective view of the structure of the complex **2** (atoms are drawn with 30% probability ellipsoids)

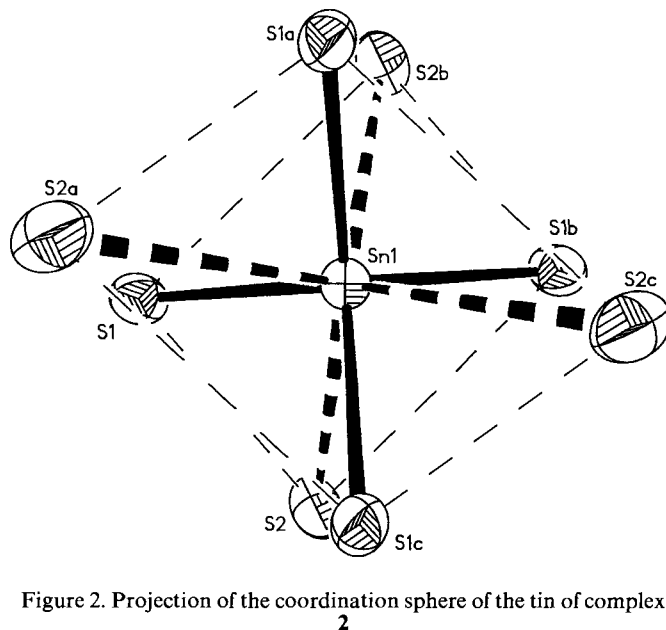


Figure 2. Projection of the coordination sphere of the tin of complex **2**

The structure of **2** is undoubtedly favored by the spatial arrangement of the ligand sulfur atoms as similar structural features have thus far not been observed in any of the previously studied complexes of Sn(IV). In the tetraacetate

$\text{Sn}(\text{O}_2\text{CMe})_4$ , for example, acetate acts as a bidentate ligand, producing a dodecahedral arrangement with almost equal Sn–O bond lengths ranging from 2.13 to 2.29 Å<sup>[13]</sup>. In tin(IV) nitrate,  $\text{Sn}(\text{O}_2\text{NO})_4$ , the geometry is also dodecahedral, and the nitrate groups are equivalent, each being symmetrically bidentate with mean Sn–O bond distances of 2.16 Å<sup>[14]</sup>. The structures of  $\text{Sn}(\text{O}_2\text{CMe})_4$  and  $\text{Sn}(\text{O}_2\text{NO})_4$  are evidently determined by the proximity of the ligating carboxylate and nitrate oxygen atoms and by the higher polarity of the Sn–O bonds.

Table 2. Selected geometrical data of complex 2. Sulfur atoms designated 1, 1a, b, c as in Figure 1

Bond distances (Å)			
Sn(1)–S(1,1a,b,c)	2.436 (1)	Sn(1)–S(2,2a,2b,c)	3.599 (1)
S(1)–C(1)	1.788 (3)	S(2)–C(2)	1.759 (3)
S(2)–C(3)	1.785 (5)	C(1)–C(2)	1.342 (5)
C(1)–C(1)	1.481 (5)	C(2)–C(21)	1.497 (5)

Bond Angles (deg)			
S(1)–Sn(1)–S(1a)	107.0 (1)	S(1)–Sn(1)–S(1b)	114.5 (1)
S(1a)–Sn(1)–S(1b)	107.0 (1)	S(1)–Sn(1)–S(1c)	107.0 (1)
S(1a)–Sn(1)–S(1c)	114.5 (1)	S(1b)–Sn(1)–S(1c)	107.0 (1)
Sn(1)–S(1)–C(1)	103.9 (1)	C(2)–S(2)–C(3)	104.9 (2)
S(1)–C(1)–C(2)	120.0 (3)	S(1)–C(1)–C(11)	116.0 (2)
C(2)–C(1)–C(1)	124.0 (3)	S(2)–C(2)–C(1)	119.1 (3)
S(2)–C(2)–C(21)	118.5 (2)	C(1)–C(2)–C(21)	122.4 (3)
S(1)–Sn(1)–S(2c)	160.4 (3)	S(2)–Sn(1)–S(1b)	160.4 (3)
S(2)–Sn(1)–S(2a)	125.9 (3)	S(2)–Sn(1)–S(2b)	80.1 (2)
S(2)–Sn(1)–S(2c)	80.1 (2)	S(2)–Sn(1)–S(2d)	125.9 (3)

Effects of bond polarity<sup>[8,9]</sup> due to the presence of the Sn–Cl bonds in the molecule also explain why tin adopts a hexacoordinated structure in **3**, wherein the (methylthio)stilbenethiolato ligands are close to being symmetrically bidentate, and the coordinate Sn–S(CH<sub>3</sub>) bonds of 2.71(2) Å are longer than the covalent Sn–S bonds of 2.46 Å (see Table 3). One thioether sulfur atom, S(4), and one chlorine atom, Cl(2) (Figure 3) are in axial positions and form an angle of 168.1(1)° with the tin atom, while Cl(1) and the other three sulfur atoms are in equatorial positions, thus realizing an essentially octahedral geometry.

While conventional hexacoordination is still favored in **3** because of the presence of the polar Sn–Cl bonds, this is no

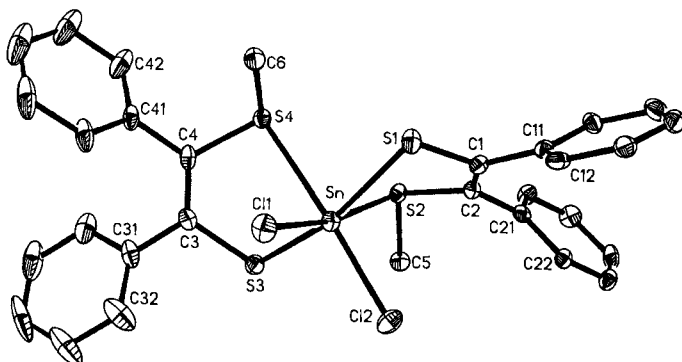


Figure 3. Perspective view of the structure of the complex **3** (atoms are drawn with 30% probability ellipsoids)

longer the case in the diphenyl derivative  $\text{Ph}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (**4**), whose structure (Figure 4, Table 4) may be described as consisting of a distorted tetrahedron made up by the covalent Sn–S and Sn–C bonds of 2.452(1) and 2.130(4) Å, respectively, and two outer-sphere coordinative Sn–S(CH<sub>3</sub>) bonds of 3.500(2) Å with an S–Sn–S bond angle of 87.2°. The four Sn–S bonds also form a distorted tetrahedron.

Table 3. Selected geometrical data of complex **3**

Bond Distances (Å)			
Sn–S(1)	2.450 (2)	Sn–S(2)	2.709 (2)
Sn–S(3)	2.461 (2)	Sn–S(4)	2.731 (2)
Sn–Cl(1)	2.398 (2)	Sn–Cl(2)	2.396 (2)
S(1)–C(1)	1.778 (5)	S(2)–C(2)	1.781 (5)
S(2)–C(5)	1.817 (5)	S(3)–C(3)	1.767 (5)
S(4)–C(4)	1.784 (5)	S(4)–C(6)	1.816 (6)
Cl(3)–C(7)	1.701 (12)	Cl(4)–C(7)	1.600 (11)
C(1)–C(2)	1.352 (7)	C(1)–C(11)	1.490 (7)
C(2)–C(21)	1.474 (7)	C(3)–C(4)	1.351 (7)

Bond Angles (deg)			
S(1)–Sn–S(2)	76.5 (1)	S(1)–Sn–S(3)	157.5 (1)
S(2)–Sn–S(3)	87.1 (1)	S(1)–Sn–S(4)	86.6 (1)
S(2)–Sn–S(4)	82.8 (1)	S(3)–Sn–S(4)	76.0 (1)
S(1)–Sn–Cl(1)	95.8 (1)	S(2)–Sn–Cl(1)	169.7 (1)
S(3)–Sn–Cl(1)	98.4 (1)	S(4)–Sn–Cl(1)	90.1 (1)
S(1)–Sn–Cl(2)	100.5 (1)	S(2)–Sn–Cl(2)	89.6 (1)
S(3)–Sn–Cl(2)	94.6 (1)	S(4)–Sn–Cl(2)	168.1 (1)
Cl(1)–Sn–Cl(2)	98.6 (1)	Sn–S(1)–C(1)	101.4 (2)
Sn–S(2)–C(2)	96.2 (2)	Sn–S(2)–C(5)	105.7 (2)
C(2)–S(2)–C(5)	104.3 (2)	Sn–S(3)–C(3)	100.9 (2)
Sn–S(4)–C(4)	95.5 (1)	Sn–S(4)–C(6)	106.8 (2)
C(4)–S(4)–C(6)	103.6 (2)	S(1)–C(1)–C(2)	124.0 (4)
S(1)–C(1)–C(11)	112.3 (4)	C(2)–C(1)–C(11)	123.7 (4)
S(2)–C(2)–C(1)	118.5 (4)	S(2)–C(2)–C(21)	115.9 (4)
C(1)–C(2)–C(21)	125.5 (5)	S(3)–C(3)–C(4)	124.3 (4)
S(3)–C(3)–C(31)	112.8 (3)	C(4)–C(3)–C(31)	122.9 (4)
S(4)–C(4)–C(3)	118.5 (4)	S(4)–C(4)–C(41)	116.2 (4)
C(3)–C(4)–C(41)	125.3 (5)	Cl(3)–C(7)–Cl(4)	117.5 (6)

The structure of **4** differs from that of  $\text{Me}_2\text{Sn}[(\text{S}_2\text{CNET}_2)_2]$ , which only shows four nearly equal short Sn–S bonds ranging from 2.525 to 2.497 Å<sup>[8]</sup>, although the S–Sn–S and C–Sn–C bond angles of 87.2(1) and 125.0° are the same.

In the triphenylstannyl derivative  $\text{Ph}_3\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]$  (**5**), the tin is almost perfectly tetrahedral and the Sn–S bond length is 2.425(3) Å (Figure 5, Table 5). The –SCH<sub>3</sub> group is in a non-interacting position. This is in contrast to  $\text{Ph}_3\text{SnS}_2\text{CN}[\text{CH}_2]_4$ , in which tin is pentacoordinated, and the dithiocarbamate ligand is bidentate with one short Sn–S bond of 2.481 Å and one elongated bond of 2.919 Å, respectively<sup>[15]</sup>. The dithiocarbamate ligand in  $\text{Ph}_3\text{SnS}_2\text{CN}[\text{CH}_2]_4$  is evidently strongly bidentate and by virtue of its stronger coordinative Sn–S interactions forces the realization of a nearly classical pentacoordinated structure. Tin is also pentacoordinated in triphenyltin-8-quinolinsulfide (triphenyltin-8-quinolinsulfide), which crystallizes in two crystallographically independent forms in which the conformations are slightly different<sup>[16]</sup>. In both conformers the S atom is in an equatorial position, and the Sn–S bond lengths are 2.441(3) and 2.427(3) Å, respectively. The axial coordinative Sn–N bonds of 2.592(9) and 2.611(8) Å are greater than the sum of the covalent radii but shorter

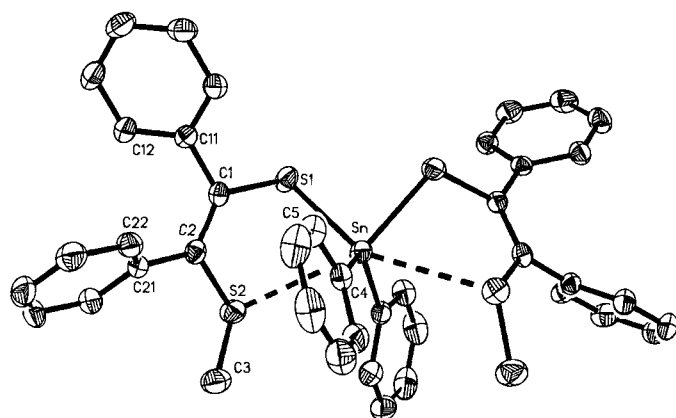


Figure 4. Perspective view of the structure of the complex 4 (atoms are drawn with 30% probability ellipsoids)

Table 4. Selected geometrical data of complex 4. Atoms designated 1a, 2a, etc. correspond to the symmetry-equivalent atoms designated 1, 2, etc. in Figure 4

Bond Distances (Å)			
Sn-S(2)	3.308 (1)	Sn-S(2a)	3.308 (1)
Sn-S(1)	2.452 (1)	Sn-S(1a)	2.452 (1)
Sn-C(1)	2.130 (4)	Sn-C(4a)	2.130 (4)
S(1)-C(1)	1.783 (3)	S(2)-C(2)	1.766 (4)
S(2)-C(3)	1.807 (4)	C(1)-C(2)	1.353 (5)
C(1)-C(11)	1.483 (5)	C(2)-C(21)	1.491 (4)

Bond Angles (deg)			
S(1)-Sn-S(2)	66.9 (1)	S(1)-Sn-S(2a)	66.9 (1)
S(1)-Sn-S(1a)	87.2 (1)	S(1)-Sn-C(4)	107.1 (1)
S(1)-Sn-C(4a)	112.0 (1)	C(4)-Sn-S(1a)	112.0 (1)
C(2)-S(2)-C(3)	107.1 (1)	C(4)-Sn-C(4a)	125.0 (2)
S(1)-C(1)-C(11)	104.6 (2)	Sn-S(1)-C(1)	106.5 (1)
S(2)-C(2)-C(1)	104.6 (2)	S(1)-C(1)-C(2)	123.3 (3)
C(1)-C(2)-C(21)	122.9 (3)	S(2)-C(2)-C(21)	118.5 (3)
Sn-C(4)-C(9)	122.0 (3)	Sn-C(4)-C(5)	120.0 (3)

than the sums of the van der Waals radii. Evidently, in complexes where tetra- and pentacoordinated structures are possible the energy differences between the possible structures are quite small. This also follows from the results of a study<sup>[17]</sup> of substituted benzoates of triphenyltin, for which

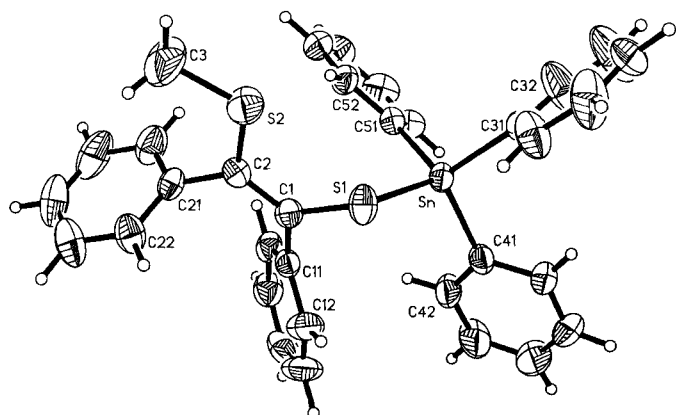


Figure 5. Perspective view of the structure of the complex 5 (atoms are drawn with 30% probability ellipsoids)

both tetrahedral and pentacoordinate *trans*-SnPh<sub>3</sub>O<sub>2</sub> polymeric structures are realized. Which of the structures is preferred for these compounds appears to depend on a delicate balance between electronic and steric influences.

Table 5. Selected geometrical data of complex 5

Bond Distances (Å)			
Sn-S(1)	2.425 (3)	Sn-C(31)	2.143 (8)
Sn-C(41)	2.136 (8)	Sn-C(51)	2.121 (8)
S(1)-C(1)	1.765 (8)	S(2)-C(2)	1.766 (9)
S(2)-C(3)	1.769 (11)	C(1)-C(2)	1.367 (10)
C(1)-C(11)	1.484 (11)	C(2)-C(21)	1.487 (10)

Bond Angles (deg)			
S(1)-Sn-C(31)	101.0 (2)	S(1)-Sn-C(41)	113.6 (2)
C(31)-Sn-C(41)	108.4 (3)	S(1)-Sn-C(51)	107.6 (2)
C(31)-Sn-C(51)	114.6 (3)	C(41)-Sn-C(51)	111.3 (3)
Sn-S(1)-C(1)	103.1 (2)	C(2)-S(2)-C(3)	105.2 (5)
S(1)-C(1)-C(2)	117.5 (6)	S(1)-C(1)-C(11)	118.5 (5)
C(2)-C(1)-C(11)	123.9 (7)	S(2)-C(2)-C(1)	119.3 (6)
S(2)-C(2)-C(21)	118.9 (5)	C(1)-C(2)-C(21)	121.6 (7)
C(1)-C(11)-C(12)	120.5 (8)	C(1)-C(11)-C(16)	121.1 (7)

Within the present context the structure of the compound PhSn[Ph(S)C=C(SCH<sub>3</sub>)Ph]<sub>3</sub> is of obvious interest. It could turn out to contain penta-, hexa-, or heptacoordinated tin with 1–3 outer-sphere coordinate Sn–S(CH<sub>3</sub>) bonds giving rise to unusual coordination geometries. The synthesis and structure of this compound along with the isoelectronic derivatives of arsenic and antimony will be described in a forthcoming paper.

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## Experimental

<sup>1</sup>H NMR: GE QE-300, 300 MHz. – IR: Perkin-Elmer 1330. – MS: Hewlett-Packard 5988 Extended Mass System. – UV-Vis: Beckman DU-40. – The ligand Ph(SH)C=C(SCH<sub>3</sub>)Ph (**1**) was synthesized by chemical degradation of the (*S*-methylthiolene)nickel complex Ni(CH<sub>3</sub>S<sub>2</sub>C<sub>2</sub>Ph)<sub>2</sub> in an alkaline solution of NaCN, as described in ref.<sup>[3]</sup>

Sn[Ph(S)C=C(SCH<sub>3</sub>)Ph]<sub>4</sub> (**2**): SnCl<sub>2</sub> · 2 H<sub>2</sub>O (0.129 g, 0.57 mmol), mixed with 20 ml of distilled water in a 50-ml beaker to form a white cloudy suspension, was added slowly to a stirred solution of **1** (0.59 g, 2.28 mmol) in 20 ml of ethanol, in a beaker of 100 ml capacity. A red-orange suspension gradually formed in the course of about 30 min which was collected by filtration and vacuum-dried. After dissolution in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> followed by the addition of hexane, 0.46 g (70%) of red prismatic crystals were obtained, m.p. 198 °C. – C<sub>60</sub>H<sub>52</sub>S<sub>8</sub>Sn (1148.3); calcd. C 62.76, H 4.56; found C 62.90, H 4.63. – MS, *m/z* (%): 514 (1) [M – SnL<sub>2</sub>], 275 (20) [M – SnL<sub>3</sub>]. – IR (Sn–S) (cm<sup>-1</sup>) in Nujol: 323. – UV-Vis [nm (ε), CH<sub>2</sub>Cl<sub>2</sub>]: 315 (350); 412 (9130). – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.75 (s, 12H, CH<sub>3</sub>), 7.25–6.91 (m, 40H, Ph).

SnCl<sub>2</sub>[Ph(S)C=C(SCH<sub>3</sub>)Ph]<sub>2</sub> (**3**): A freshly prepared 2 M solution of SnCl<sub>4</sub> in anhydrous CH<sub>2</sub>Cl<sub>2</sub> was placed into a syringe, and 0.25 ml of this solution (0.50 mmol) was added slowly to 10 ml of a solution of 0.258 g (**1**, 1.0 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> in a medium-sized Schlenk tube with strong stirring. On addition of 20 ml of

hexane to the upper layer a red-orange precipitate formed overnight which was collected by filtration and vacuum-dried. After recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane, 0.30 g (0.42 mmol, 85%) of red-orange rectangular crystals were obtained, m.p. 165°C. —  $\text{C}_{30}\text{H}_{26}\text{Cl}_2\text{S}_4\text{Sn}$  (704.4): calcd. C 51.15, H 3.72; found C 51.04, H 3.81. — MS,  $m/z$  (%): 514 (3) [M — SnL<sub>2</sub>], 275 (52) [M — SnL<sub>3</sub>]. — IR (Sn—S) ( $\text{cm}^{-1}$ ) in Nujol: 370. — UV-Vis [nm ( $\epsilon$ ),  $\text{CH}_2\text{Cl}_2$ ]: 320 (18440), 400 (5165). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 2.31 (s, 6H, CH<sub>3</sub>), 7.26–7.07 (m, 20H, Ph).

$\text{Ph}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (4): A solution of 0.344 g (1.0 mmol) of  $\text{Ph}_2\text{SnCl}_2$  in 20 ml of ethanol was added to 20 ml of a stirred, hot ethanolic solution containing 0.516 g (2.0 mmol) of **1** in a medium-size Schlenk tube. Upon cooling a yellow precipitate formed which was collected by filtration and vacuum-dried. After recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane, 0.65 g (0.82 mmol, 82%) of yellow plate-like crystals were obtained, m.p. 149°C. —  $\text{C}_{42}\text{H}_{36}\text{S}_4\text{Sn}$  (787.7): calcd. C 64.04, H 4.61; found C 64.30, H 4.50. — MS,  $m/z$  (%): 531 (2) [M — L], 257 (4) [M — SnL<sub>2</sub> — Ph]. — IR (Sn—S) ( $\text{cm}^{-1}$ ) in Nujol: 351. — UV-Vis [nm ( $\epsilon$ ),  $\text{CH}_2\text{Cl}_2$ ]: 332 (9020). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.61 (s, 6H, CH<sub>3</sub>), 6.56–7.00 (m, 10H, Ph), 7.36–7.70 (m, 20H, Ph).

$\text{Ph}_3\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]$  (5): A solution of  $\text{Ph}_3\text{SnCl}$  (0.770 g, 2.0 mmol) in 20 ml of ethanol was added to 0.516 g (2.0 mmol) of **1** in 20 ml of ethanol in a medium-sized Schlenk tube with vigorous stirring. The reaction mixture was cooled to 0°C. Within 3 h the originally yellow precipitate converted into a colorless microcrystalline solid. This was collected by filtration, vacuum-dried, and recrystallized from  $\text{CH}_2\text{Cl}_2$ /CH<sub>3</sub>OH, affording 0.96 g (1.58 mmol, 79%) of **5**, m.p. 126°C. —  $\text{C}_{33}\text{H}_{28}\text{S}_2\text{Sn}$  (607.4): calcd. C 65.25, H 4.65; found C 65.14, H 4.71. — MS,  $m/z$  (%): 531 (2) [M — L], 257 (4) [M — SnL — 2 Ph]. — IR (Sn—S) ( $\text{cm}^{-1}$ ) in Nujol: 335. — UV-Vis [nm ( $\epsilon$ ),  $\text{CH}_2\text{Cl}_2$ ]: 320 (7880). —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 1.64 (s, 3H, CH<sub>3</sub>), 6.59–7.01 (m, 15H, Ph), 7.34–7.57 (m, 10H, Ph).

*X-ray Characterization of  $\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_4$  (2):* A red prismatic single crystal of the dichloromethane-solvated complex **2** was put on a glass fiber along the longest dimension and then mounted on a Siemens R 3m/V diffractometer for X-ray data collection employing the Siemens SHELXTL PLUS (MicroVAX II) System. Background measurement was performed with stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time, with 3 standard reflections measured every 100 reflections over index ranges  $0 < h < 24$ ,  $0 < k < 24$ ,  $0 < l < 19$ . The number of reflections observed and other details of the structure determination are summarized in Table 1, additional information is given in the supplementary material. The intensities of monitor reflections decreased by approximately 25% during 44 h of X-ray of exposure. No absorption correction was applied because of low value of  $\mu$ . The unit cell parameters were obtained from 28 reflections in the range of  $15 < 2\theta < 30^\circ$ . The space group was identified as  $I4_1/a$  (No. 88,  $C_4^2$ ). — The tin atom present in the special position showed a four-site symmetry from the automatic direct methods routine of the program SHELXTL PLUS. The positions of the remaining non-hydrogen atoms were determined from a difference Fourier map. All atoms except C and

Cl atoms of the solvent were refined anisotropically. Hydrogen atoms were included in ideal positions with  $U$  fixed at  $0.08 \text{ \AA}^2$ . Refinements gave final values of  $R$  and  $wR$  which are given in Table 1. The final difference map had no feature of any chemical significance, though it had a few residual peaks with density  $0.30 \text{ e \AA}^{-3}$ . No evidence of secondary extinctions was found, therefore no correction applied.

*X-ray Characterizations of  $\text{SnCl}_2[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (3),  $\text{Ph}_2\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]_2$  (4), and  $\text{Ph}_3\text{Sn}[\text{Ph}(\text{S})\text{C}=\text{C}(\text{SCH}_3)\text{Ph}]$  (5):* The crystals of these complexes were mounted on a Siemens R3m/V diffractometer for X-ray data collection. The space groups of the compounds are given in Table 1. The tin atoms of these complexes were determined from the automatic direct methods routine of the program SHELXTL PLUS. No absorption corrections were applied. The position of the remaining non-hydrogen atoms were determined from a difference Fourier map. All atoms were refined anisotropically. Hydrogen atoms were included in ideal positions with  $U$  fixed at  $0.08 \text{ \AA}^2$ . Refinements gave final values of  $R$  and  $wR$  (Table 1).

Supplementary X-ray structural data may be obtained from the Fachinformatinszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. Please include the depository number CSD-57475, the names of the authors, and the journal citation.

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